

Amino-Aryl-Carbenes: Alternative Ligands for Transition Metals?

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In the last 10 years spectacular achievements have been made in the area of catalysis using N-heterocyclic carbenes (NHCs) as strong σ -donor ligands for transition metals.^{1,2} Although NHC complexes have been known since the 1960s,³ these recent developments have only been made possible because of the availability of *stable* carbenes **A–C**.⁴ However, the great structural diversity, which is a great strength of phosphorus-based ligands, is far from being available with carbene-based ligands since, apart from NHCs **A–C**, only a few types of carbenes are believed to be stable. Accordingly, the tuning of their stereo-electronic properties has thus far only been achieved by slight modifications of the ring framework, as exemplified by **D–F**,^{5–7} the only exception being the acyclic diamino-carbenes **G**⁸ (Figure 1). Significantly, the latter have been demonstrated to be even stronger σ -donor ligands than their cyclic counterparts.⁹

We have recently shown that, despite the presence of a single amino group, carbenes **H** featuring the bulky 2,4,6-tri(*tert*-butyl)phenyl (Mes*) and 2,6-bis(trifluoromethyl)phenyl (Ar_F) substituents can be characterized or even isolated.¹⁰ Here we report the synthesis of a less sterically hindered amino-aryl-carbene, which gives us the opportunity to investigate its coordination behavior toward transition metals.¹¹

Aiming at reducing the steric hindrance around the carbene center, the anthryl group, which was successfully used by Tomioka et al. for the stabilization of triplet carbenes,¹² has been chosen. The iminium salt **1** was readily prepared in 58% yield as a yellow crystalline solid by condensation of 9-anthraldehyde with *tert*-butylamine and subsequent alkylation with methyl trifluoromethanesulfonate. Deprotonation of **1** with potassium *tert*-butoxide in THF at -78 °C led to a bright orange color that rapidly vanished upon warming to room temperature. After workup, the aminoral **3** was isolated in 95% yield as a pale-yellow oil. However, monitoring the reaction by ¹³C NMR at -50 °C allowed the identification and characterization of the desired carbene **2**¹³ ($\delta^{13}\text{C}$ 315 ppm). Whereas carbenes **H** featuring Mes* and Ar_F substituents were found to be inert toward *tert*-butyl alcohol,¹⁰ carbene **2** inserted into the O–H bond within a few minutes at -35 °C, demonstrating the significantly lower steric protection caused by the anthryl group (Scheme 1).

This O–H insertion reaction could be avoided by deprotonation of **1** with the lithium salt of hexamethyldisilazane or mesityllithium. Under these conditions, the amino-anthryl-carbene **2** is stable for days in solution at -30 °C, and has a half-life of about 12 h at 4 °C (as measured by ¹H NMR with an internal standard). Carbene **2** was efficiently trapped by boron trifluoride in THF. Yellow monocrystals of the adduct **4** (67% yield), suitable for an X-ray diffraction study,¹⁴ were obtained from a saturated toluene solution at 4 °C (Figure 2). As expected because of the presence of a single

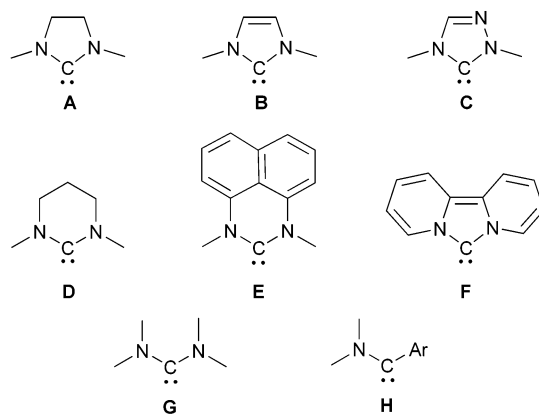
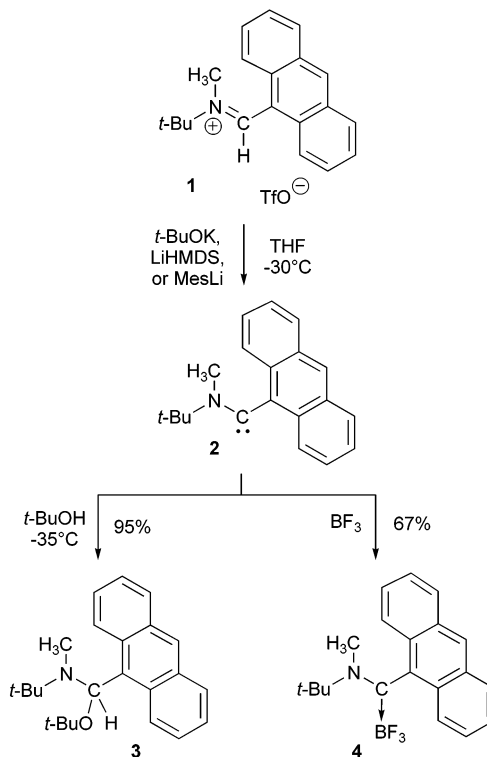


Figure 1. Schematic representation of stable carbenes **A–H**.

Scheme 1



electron-donating amino substituent, the C–N bond is significantly shorter in **4** (1.301(2) Å) than in the related NHC–BF₃ adducts¹⁵ (1.34–1.36 Å), but the C_{carbene}–B bond distance is only slightly longer (1.688(3) Å compared to 1.63–1.67 Å).

To test its coordination ability, carbene **2** was treated with 0.5 equiv of bis(μ -chloronorbornadiene-rhodium) at -60 °C (Scheme 2).¹⁶ After workup, complex **5** was isolated as highly thermally

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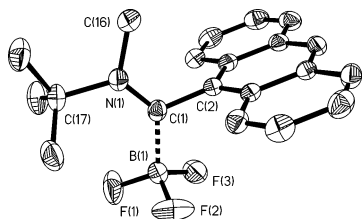


Figure 2. Thermal ellipsoid diagram (50% probability) of **4** (H atoms are omitted). Selected bond distances (Å) and angles (deg): N(1)–C(1) 1.301(2), C(1)–B(1) 1.688(3), N(1)–C(1)–C(2) 116.57(17), N(1)–C(1)–B(1) 132.81(17), C(2)–C(1)–B(1) 110.59(15).

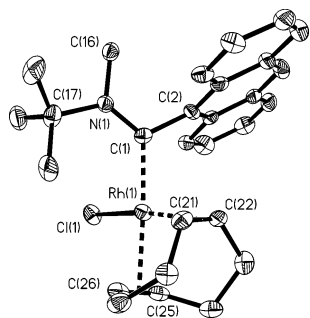
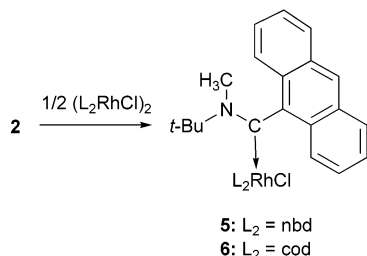


Figure 3. Thermal ellipsoid diagram (50% probability) of **6** (H atoms are omitted). Selected bond distances (Å) and angles (deg): N(1)–C(1) 1.326(9), C(1)–Rh(1) 2.043(7), Rh(1)–C(21) 2.127(8), Rh(1)–C(22) 2.134(7), Rh(1)–C(25) 2.250(8), Rh(1)–C(26) 2.216(8), N(1)–C(1)–C(2) 114.8(6), N(1)–C(1)–Rh(1) 128.5(5), C(2)–C(1)–Rh(1) 116.7(5).

Scheme 2



stable single crystals (mp 190–191 °C). The ¹³C NMR signal for the carbene center of **5** appears at 264 ppm as a doublet (¹J_{CRh} = 45 Hz). This chemical shift is 50 ppm downfield from that of the free carbene **2**, but still significantly upfield from those of diamino-carbene–rhodium complexes (180–234 ppm).

To evaluate the electron-donating ability of carbene **2**, the RhCl(cod)(carbene) complex **6** was prepared,¹⁷ and its geometric parameters (Figure 3) were compared with those of the corresponding complexes featuring diamino-carbenes **A**,¹⁸ **B**,¹⁹ **C**,²⁰ **E**,⁶ or **G**.⁹ The monoamino-carbene complex **6** features the shortest C–N bond of the series (1.326(9) Å compared to 1.35–1.36 Å), but a C_{carbene}–Rh bond length within the typical range (2.043(7) Å compared to 2.00–2.06 Å). Notably, the Rh–C_{cod} bonds trans to the carbene ligand are significantly elongated in **6** (Rh–C_{trans} 2.23 Å, Rh–C_{cis} 2.13 Å), the magnitude of this phenomenon (about 10 pm) is again very similar to that observed for diamino-carbenes.

These results as a whole demonstrate that despite the presence of a single amino substituent, the amino-anthryl-carbene **2** behaves as a strong σ-donor/weak π-acceptor ligand. Monoamino-carbenes might therefore be considered as valuable alternatives to diamino-carbenes. Their stereo-electronic properties could be tuned by varying the nature of the second substituent (aryl/alkyl, electron-rich/-poor), and further studies in this direction are currently in progress.

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Supporting Information Available: Full experimental details, spectroscopic data (PDF) and X-ray crystallographic data for **1–6** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (13) Iminium salt **1** (80 mg, 0.19 mmol) was added at –78 °C to a THF-*d*₈ solution (0.75 mL) of lithium hexamethyldisilazane (46 mg, 0.19 mmol). The orange solution was warmed to –50 °C and analyzed by NMR spectroscopy. ¹H NMR (THF-*d*₈, 223 K): δ 1.74 (s, 9 H, tBu), 3.08 (s, 3 H, CH₃), 7.25–7.35 (m, 2 H, H_{arom}), 7.4–7.5 (m, 4 H, H_{arom}), 7.93 (d, 2 H, ³J_{HH} = 8.4 Hz, H_{arom}), 7.99 (s, 1 H, H_{para}); ¹³C{¹H} NMR (THF-*d*₈, 223 K): δ 28.9 [C(CH₃)₃], 37.2 (CH₃), 66.1 [C(CH₃)₃], 117.9 (C_{arom}), 119.3 (CH_{para}), 123.5 (CH_{arom}), 125.6 (CH_{arom}), 125.7 (CH_{arom}), 128.7 (CH_{arom}), 132.4 (C_{arom}), 144.1 (C_{ipso}), 315.0 (C_{carb}).
- (14) Crystal data for **4**: C₂₀H₂₁BF₃N, *M* = 343.19, orthorhombic, space group *Pbca*, *a* = 12.5095(9) Å, *b* = 13.2254(10) Å, *c* = 20.9777(16) Å, *V* = 3470.6(4) Å³, *Z* = 8, μ(Mo Kα) = 0.098 mm^{–1}, crystal size = 0.2 × 0.4 × 0.6 mm³, 19108 reflections collected (3568 independent, *R*_{int} = 0.0551), 230 parameters, *R*1 [*I* > 2σ(*I*)] = 0.0451, *wR*2 [all data] = 0.1111. For **6**: C₂₈H₃₃ClNRh, *M* = 521.91, monoclinic, space group *P2₁/n*, *a* = 11.154(3) Å, *b* = 14.840(3) Å, *c* = 14.405(3) Å, β = 94.718(4)°, *V* = 2376.2(10) Å³, *Z* = 4, μ(Mo Kα) = 0.847 mm^{–1}, crystal size = 0.2 × 0.3 × 0.4 mm³, 10287 reflections collected (3404 independent, *R*_{int} = 0.0842), 296 parameters, *R*1 [*I* > 2σ(*I*)] = 0.0550, *wR*2 [all data] = 0.1307. Data were collected at 173(2) K using an oil-coated shock-cooled crystal on a Bruker-AXS CCD 1000 diffractometer. Semiempirical absorption corrections were employed.²¹ The structures were solved by direct methods (SHELXS-97),²² and refined using the least-squares method on *F*².²³ Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-228205 (**4**), 228206 (**5**) and 228207 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk].
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